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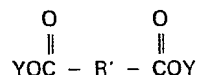
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(54) **Two-stage process for producing polybenzimidazoles from dicarboxylic component.**

(57) A two stage process for the production of polybenzimidazoles is provided wherein an aromatic tetraamine, e.g., 3,3',4,4' - tetraaminobiphenyl is reacted with a free dicarboxylic acid, e.g., isophthalic acid, or with a dicarboxylic component comprising a compound having the formula



in which R' is a divalent organic radical and Y is hydrogen, aryl or alkyl provided that no more than 95% of the Y's are hydrogen or phenyl. The reactants are heated with agitation in a first stage to a temperature above the melting point of the tetraamine until the viscosity of the mixture rises as indicated by an agitator torque of at least 1.5 times that before the rise in viscosity. The agitation is then discontinued and the reaction mixture is allowed to foam while heating is continued. The foam is then allowed to cool to a friable mass and is crushed to a ground prepolymer which is heated with agitation in a second stage until the desired polymer is obtained. The invention makes possible the production of certain new polybenzimidazoles.

BACKGROUND OF THE INVENTION

5 The present invention provides a two-stage melt polymerization process for the production of high molecular weight polybenzimidazoles utilizing a free aromatic dicarboxylic acid as monomer.

0 High molecular weight polybenzimidazoles are polymers of high thermal stability and excellent resistance to oxidative or hydrolytic degradation, which can be formed into shaped articles such as fibers and films having very desirable physical properties. As taught by the published literature, these polymers may be prepared, for example, by melt polymerizing an aromatic tetraamine and a diphenylester or an anhydride of an aromatic or heterocyclic dicarboxylic acid in a one or two stage process; see, for example H.Vogel and C.S. Marvel, Journal of Polymer Science, Vol.L, pages 511-539 (1961); and U.S. Patents Reissue 26,065; 3,174,947; 3,509,108; 3,551,389; 3,433,772; and 3,655,632. In particular, U.S. Patent 3,555,389 discloses a two-stage process for the production of aromatic polybenzimidazoles, in which the monomers are heated at a temperature above 170°C. in a first stage melt polymerization zone until a foamed prepolymer is formed.

5 The foamed prepolymer is cooled, pulverized, and introduced into a second stage polymerization zone where it is heated again to yield a polybenzimidazole polymer product.

0 It has also been known to prepare polybenzimidazoles from the free dicarboxylic acids or the methyl esters of such acids rather than the phenyl esters or anhydrides in a melt polymerization process. However, many of the early investigators of these polymers believed that inferior or unsatisfactory polymers resulted from the use of the free acid or the dimethyl ester as the monomer. Thus Vogel and Marvel state in their cited article at page 513 that in attempting to prepare polybenzimidazoles from aromatic dioic acids or

their dimethyl esters and aromatic tetraamines, "The use of the free acids and the corresponding dimethyl esters gave inferior results." Moreover, these same two investigators do not mention the free acids or dimethyl esters as monomers in their U.S. Patent No. 3,174,947 in which polybenzimidazoles are disclosed and claimed, nor are the free acids or dimethyl esters mentioned as possible monomers in any of the other cited patents.

In addition to the melt polymerization process described in the foregoing references, a process of preparing polybenzimidazoles has been proposed in which good results are reported to be obtained using a free dicarboxylic acid or a dimethyl ester of such acid as monomer. This process involves the solution polymerization of an inorganic acid salt of an aromatic tetra-amine and a dicarboxylic acid or a derivative thereof such as the dimethyl ester with heat in the presence of polyphosphoric acid (see U.S. Patent 3,313,783 and Iwakura et al, Journal of Polymer Science: Part A, Vol. 2, pages 2605-2615 (1964)). According to this process, the polymer product after completion of the reaction can be separated by pouring the reaction mixture in the form of a polyphosphoric acid solution into a large quantity of water. However, this separation procedure is complicated and, moreover, it is difficult to recover and reuse the polyphosphoric acid.

Despite the disadvantages of processes utilizing a free dicarboxylic acid or methyl or other alkyl ester as monomer in the preparation of polybenzimidazoles, these materials have concomitant advantages over the phenyl esters which are the most widely taught dicarboxylic acid derivatives for the preparation of these polymers. Thus, the free acid and its alkyl esters are generally less expensive than the corresponding phenyl ester and their use does not result in the formation of free phenol as a by-product. The formation of free phenol is undesirable because of toxicity problems, and the avoidance or reduction thereof is beneficial.

5 In view of this there have been attempts to develop processes which utilize a free acid as monomer and result in polymers which can be formed into shaped articles of commercial utility. For example, U.S. Patent 4,312,976 discloses a single-stage process for preparing polybenzimidazoles from a free dicarboxylic acid as monomer, wherein the catalyst is an organic sulfonic acid, a halogenated acetic acid or a non-oxidizing inorganic acid. However, apart from being limited to a specific class of catalysts, this process results in a polymer mass of high viscosity requiring substantial agitation energy, especially in the latter part of the polymerization process. Furthermore, the final polymer is in the form of a solidified mass which is difficult to handle and to dissolve in an appropriate solvent for forming into shaped articles such as fibers.

10 The present invention provides a two stage process for the production of polybenzimidazoles which makes it possible to achieve various combinations of the advantages and relative disadvantages of the free acid, the alkyl ester and the phenyl ester, in a process which is simple and relatively efficient.

20 The free acid may be used as sole dicarboxylic component. This substantially eliminates the disadvantages of a one stage process utilizing the free acid as described previously. On the other hand, it usually results (like the known one stage process) in the formation of water contaminated with tetraamine as a by product which is difficult to dispose of.

30 An alkyl ester (for example a methyl ester) may be used as sole dicarboxylic component. This results in the formation of an alkanol (for example methanol), which allows for easy disposal by combustion of the tetraamine contaminated by product.

A combination of the free acid and an alkyl ester may be used. This provides substantially the advantages of each.

5 A phenyl ester may be used as part of the dicarboxylic component. Notwithstanding the disadvantages of such esters and the advantages of the free acid and of alkyl esters, it may be desirable sometimes to use a phenyl ester as part of the dicarboxylic component (in combination
10 with the free acid and (or the alkyl ester) to achieve some of the process advantages associated with phenyl esters.

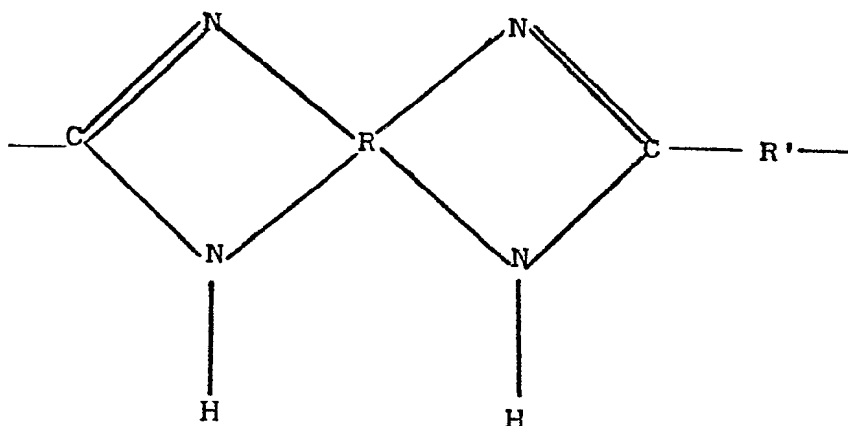
The dicarboxylic component will be more particularly defined below.

15 SUMMARY OF THE INVENTION

The invention provides a process for preparing polybenzimidazoles by reacting at least one aromatic tetra-
amine containing two pairs of amine substituents on an
20 aromatic ring, the amine substituents being ortho to one another, with a dicarboxylic component in a two stage polymerization process. In the first stage of the process, the mixture of aromatic tetraamine and dicarboxylic acid
(and, if desired, a polymerization catalyst) is heated to
25 condensation polymerization temperatures which are above the melting point of the aromatic tetraamine. Depending on the nature and melting point of the dicarboxylic component, the resulting polymerizing mass is a liquid which may be a slurry of solid dicarboxylic component particles in melted
30 tetraamine, or a homogeneous mixture of tetraamine and dicarboxylic component or an emulsion comprising melted tetraamine and melted dicarboxylic component. The heating is continued to 230-350°C with concurrent strong agitation until the viscosity of the mixture rises to a point such
35 that the agitator torque is from 1.5 times to 6 times the torque before the increases in viscosity begins to occur.

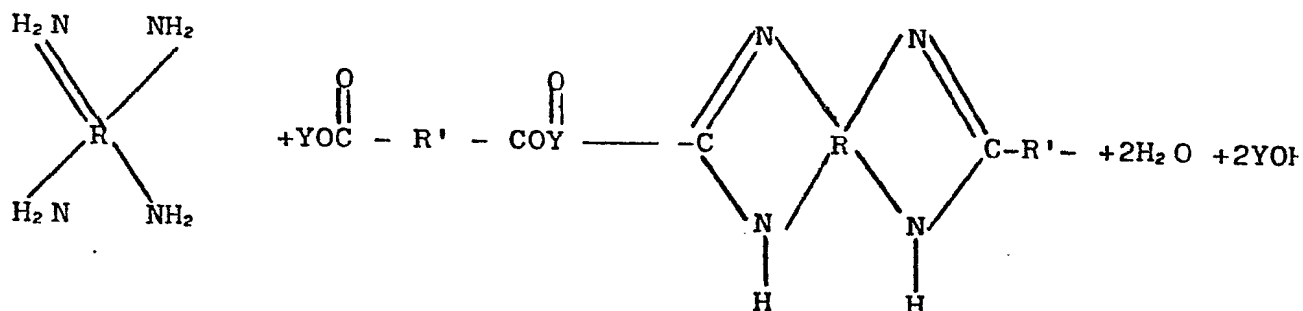
The agitation is then terminated, and heating is continued while allowing the mass to foam to a friable mass. The resulting prepolymer is then cooled and ground to a powder which is heated in the solid state in a second polymerization stage at a higher temperature than the first stage until the desired degree of polymerization is achieved.

The polybenzimidazoles which can be produced by the process of this invention are those having repeating units of the following formula:



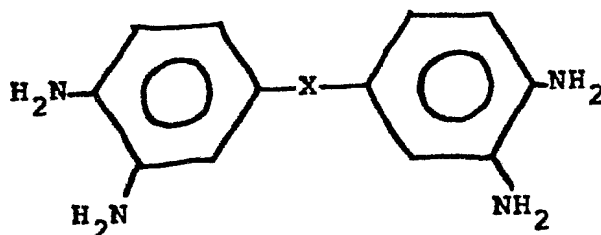
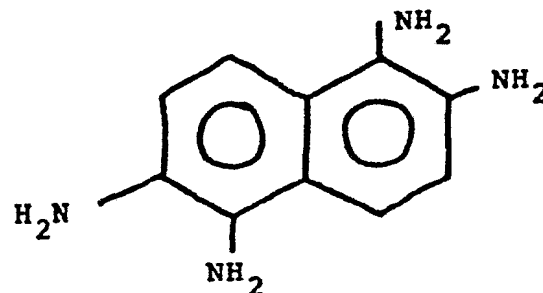
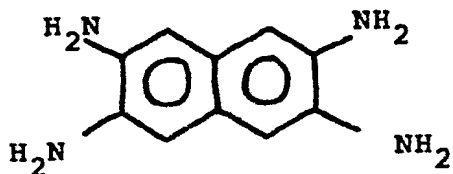
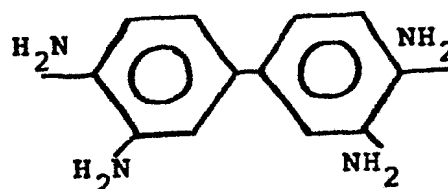
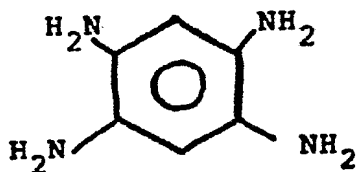
wherein R is a tetravalent aromatic nucleus with the nitrogen atoms forming the benzimidazole rings being paired upon adjacent carbon atoms, i.e., ortho carbon atoms, of the aromatic nucleus, and R' is a divalent organic radical which is usually a member of the class consisting of an aromatic ring, an alkylene group (preferably having 4 to 8 carbon atoms), and a heterocyclic ring (such as pyridine, pyrazine, furan, quinoline, thiophene, and pyran).

The following generalized equation illustrates the condensation reaction which occurs in forming the polybenzimidazoles having the recurring units of the foregoing formula:



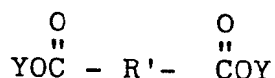
Such polybenzimidazoles may be produced by the reaction of a mixture of (1) at least one aromatic tetra-amine containing two groups of amine substituents, the amine substituents in each group being in an ortho position relative to each other, and (2) at least one dicarboxylic component as defined herein.

Examples of aromatic tetraamines which may be used include those with the following formulas:



where X represents -O-, -S-, -SO₂-, -C-, or a lower alkylene group, such as -CH₂-, -(CH₂)₂-, or -C(CH₃)₂-. Among such aromatic tetraamines may be mentioned, for example, 1,2,4,5- tetraaminobenzene; 1,2,5,6-tetra-aminonaphthalene; 2,3,6,7-tetraaminonaphthalene; 3,3',4,4' -tetraamino-diphenyl methane; 3,3',4,4' -tetraaminodiphenyl ethane; 3,3',4,4'-tetraaminodiphenyl-2,2-propane; 3,3',4,4'-tetraaminodiphenyl thioether; and 3,3',4,4' - tetraaminodiphenyl sulfone. The preferred aromatic tetraamine is 3,3',4,4' - tetraamino-biphenyl.

The dicarboxylic component is at least one dicarboxylic acid or at least one dicarboxylic compound having the formula



in which R' is a divalent organic radical and may be the same or different in various molecules making up the dicarboxylic component, and

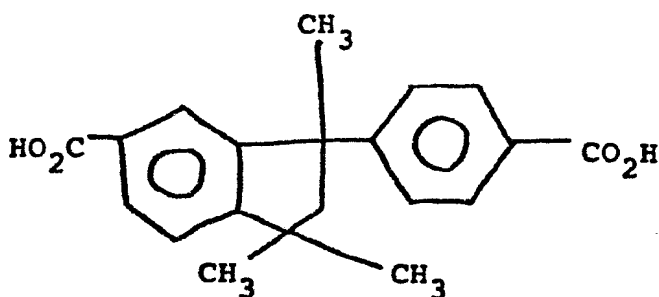
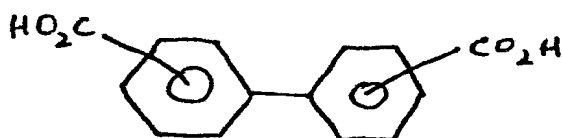
Y is hydrogen, aryl or alkyl and may be different in various molecules (or within each molecule) making up the dicarboxylic component provided that either (i) all Y's are hydrogen or (ii) all Y's are alkyl or (iii) not more than 95% of the Y's are hydrogen or phenyl.

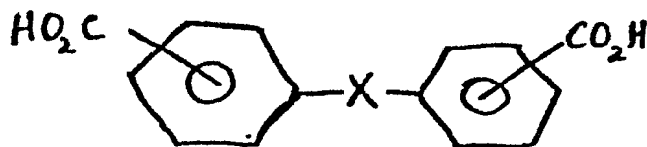
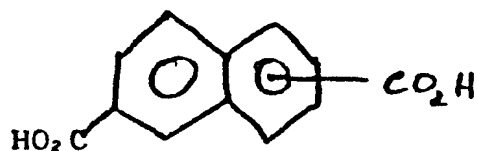
For example, the dicarboxylic component may consist of a free acid or acids ; or a mixture of a free acid or acids with at least at one diester and/or monoester; or a mixture of diester(s) and/or monoester(s); or a single dialkyl ester, monoester or mixed aryl-alkyl or alkyl/alkyl ester or esters but cannot consist solely of diphenyl ester. When Y is alkyl, it preferably contains 1 to 5 carbon atoms and is most preferably methyl. When Y is aryl, it may be any monovalent aromatic group obtained by filling with hydrogen all the valences but one of the aromatic groups which may be R or R' as disclosed previously, either unsubstituted or substituted with any inert monovalent radical such as alkyl or alkoxy

containing 1 to 5 carbon atoms. Examples of such aryl groups are phenyl, naphthyl, and three possible phenylphenyl radicals and the three possible tolyl radicals. The preferred aryl group is usually phenyl.

5 The dicarboxylic acids which are suitable for use in free or esterified form (as described above) in the production of polybenzimidazoles by the process of the present invention include aromatic dicarboxylic acids; ali-
 10 phatic dicarboxylic acids (preferably those having 4 to 8 carbon atoms); and heterocyclic dicarboxylic acids wherein the carboxyl groups are substituents upon carbon atoms in a ring compound (such as pyridine, pyrazine, furan, quino-
 line, thiophene, and pyran).

15 The preferred dicarboxylic acids which may be utilized in free or esterified form are aromatic dicarboxylic acids such as those having the following formulae:





where X is as defined above. For example, the following diacids are suitable isophthalic acid; terephthalic acid; 4,4'-biphenyldicarboxylic acid; 1,4-naphthalenedicarboxylic acid; diphenic acid 2,2'-biphenyldicarboxylic acid); phenyl-lindan; dicarboxylic acid; 1,6-naphthalenedicarboxylic acid; 2,6-naphthalenedicarboxylic acid; 4,4'-diphenylether-dicarboxylic acid; 4,4'-diphenylmethanedicarboxylic acid; 4,4'-diphenyl-sulfonedicarboxylic acid; and 4,4' diphenylthioetherdicarboxylic acid. Isophthalic acid is the dicarboxylic acid which is free or esterified form is most preferred for use in the process of the present invention.

If the dicarboxylic component is not the free acid then it is preferably one of the following:

- 1) at least one free dicarboxylic acid and at least one diphenyl ester of a dicarboxylic acid;
- 2) at least one free dicarboxylic acid and at least one dialkyl ester of a dicarboxylic acid, and
- 3) at least one diphenyl ester of a dicarboxylic acid and at least one dialkyl ester of a dicarboxylic; and
- 4) at least one dialkyl ester of a dicarboxylic acid. The dicarboxylic moieties of the compounds of each combination may be the same or different and the alkyl groups of the alkyl esters of combination 2), 3) and 4) generally contain 1 to 5 carbon atoms and are most preferably methyl.

It is generally preferred to employ the dicarboxylic component in a ratio of about 1 mole of total dicarboxylic component per mole of aromatic tetraamine. However, the optimal ratio of reactants in a particular polymerization system can be easily determined by one of ordinary skill in the art.

Examples of polybenzimidazoles which may be prepared according to the process of the present invention include:

- 10 poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole;
poly-2,2'-(biphenylene-2"2'')-5,5'-bibenzimidazole;
poly-2,2'-(biphenylene-4"4'')-5,5'-bibenzimidazole;
- 15 poly-2,2'-(1",3",3" tramethylindanylene-6",1"-phenylene-4"')-5,5'-bibenzimidazole;
poly-2,2'-(furylene-2",5")-5,5'-bibenzimidazole;
poly-2,2'-(naphthalene-1",6")-5,5'-bibenzimidazole
- 20 poly-2,2'-(amylene-5,5'-bibenzimidazole;
poly-2,2'-octamethylene-5,5'-bibenzimidazole;
poly-2,2'-(m-phenylene)-diimidazobenzene;
poly-2,2'-cyclohexenyl-5,5'-bibenzimidazole;
poly-2,2'-(m-phenylene)-5,5'-di(bibenzimidazole)
- 25 ether
poly-2,2'-(m-phenylene)-5,5'-di(bibenzimidazole)
sulfide;
poly-2,2'-(m-phenylene)-5,5'-di(bibenzimidazole)
sulfone;
- 30 poly-2,2'-(m-phenylene)-5,5'-di(bibenzimidazole)
methane;
poly-2,2"-(m-phenylene)-5,5"-di(bibenzimidazole)
propane-2,2;
poly-2,2"-(m-phenylene)-5,5"-di(bibenzimidazole)
- 35 ethylene 1,2

where the double bonds of the ethylene groups are intact in the final polymer.

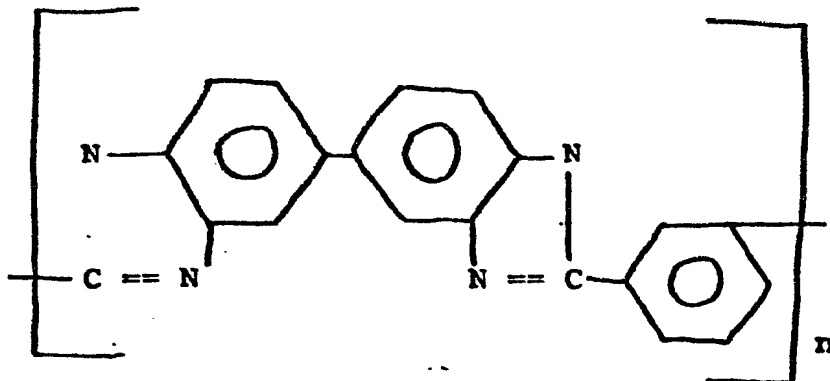
Further examples include:

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poly-2,2'-(1",1",3" trimethylindanylene-3"5"-p-phenylene-5,5'-bibenzimidazole;
2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2-(1",1",3" -trimethylindanylene)-5",3"-(p-phenylene)-5,5'-bibenzimidazole copolymer;
2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-biphenylene-2",2'') -5,5'-bibenzimidazole copolymer;
poly-2,2'-(furylene-2",5")-5,5'-bibenzimidazole;
poly-2,2'-(naphthalene-1",6")-5,5'-bibenzimidazole;
poly-2,2'-(naphthalene-2",6")-5,5'-bibenzimidazole;
poly-2,2'-amylene-5,5' -bibenzimidazole;
poly-2,2'-octamethylene-5,5' -bibenzimidazole;
poly-2,2'-(m-phenylene)-diimidazobenzene;
poly-2,2'-cyclohexenyl-5,5'bibenzimidazole;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole);
ether;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole) sulfide;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole) sulfone;
poly-2,2'-(m-phenylene)-5,5'-di(benzimidazole) propane-2,2; and
poly-ethylene-1,2-2,2'-(m-phenylene)-5,5"-dibenzimidazole) ethylene-1,2

Where the double bonds of the ethylene groups are intact in the final polymer.

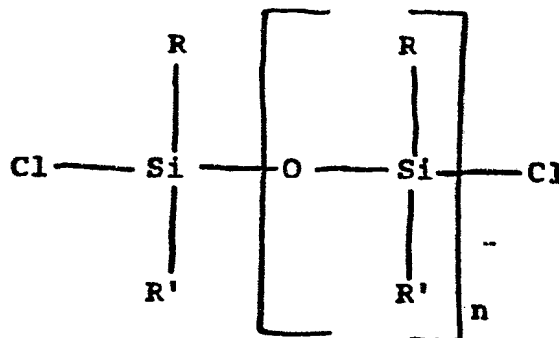
The preferred polybenzimidazole prepared by the process of the present invention is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, the recurring unit of which is:



wherein n is an integer in excess of 75.

This polymer can be prepared in accordance with the process of the present invention by the reaction of 3,3',4,4'-tetraaminobiphenyl with isophthalic acid, or with at least one dialkyl isophthlate for example dimethyl isophthalate, or with a combination of isophthalic acid and diphenyl isophthalate or dialkyl isophthalate (for example dimethyl isophthalate), or with a combination of diphenyl isophthalate and dialkyl isophthalate (for example methyl isophthalate).

The polymerization process of this invention can be carried out without a catalyst, but it is preferable to have a catalyst present in order to increase inherent viscosity. Catalysts which may be used include, for example, phosphorus compounds such as triaryl phosphites and diarylphosphites in which the aryl groups may be, for example, phenyl, tolyl or substituted phenyl wherein the substituents may be, for example, alkyl or alkoxy containing up to 4 carbon atoms, trialkyl phosphites wherein the alkyl groups contain up to 4 carbon atoms, triaryl phosphines wherein the aryl group may be phenyl, tolyl, naphthyl, fluorophenyl or methoxyphenyl, and trialkyl phosphines, wherein the alkyl groups may be propyl or butyl, halophosphines such as phenyl-dichlorophosphine, phosphorustrihalides, phosphorusoxy trihalides, magnesium, manganese and alkali metal hypophosphites, e.g. sodium hypophosphites, and triaryl phosphates, e.g. triphenyl phosphate; tin compounds such as m-butylstannic acid, dibutyltin oxide, dibutyltin acetate, stannous chloride, stannic chloride, dibutyltin dilaurate, and stannous oxalate; silanes and siloxanes of the formula:



where R and R' may be the same or different and are methyl, phenyl or hydrogen and n is zero or an integer, e.g. up to 5, such as dimethyl-dichlorosilane, diphenyldichlorosilane, methylphenyldichlorosilane, and 1,3-dichloro-1,1,3,3-tetramethylsiloxane; organic sulfonic acids such as p-toluene-sulfonic acid, benzenesulfonic acid, methanesulfonic acid, trifluoromethanesulfonic acid, and mixtures of the above, halogenated acetic acids such as trifluoroacetic acid and trichloroacetic acid, and mixtures of the above and non-oxidizing acids such as sulfuric acid, phosphoric acid or hydrochloric acid. the preferred catalyst is triphenyl phosphite.

The process of the invention may be used to produce polybenzimidazoles of one or more aromatic tetraamines and one or more dicarboxylic acids. In general, stoichiometric quantities of the total tetraamine and dicarboxylic component are utilized.

If a catalyst is employed, it is generally present in an amount, for example, of 1 to 6 mole %, preferably 2 to 4 mole %, based on the total tetraamine or dicarboxylic acid component.

The first stage of the process of the invention is carried out by heating the aromatic tetraamine and dicarboxylic component (and catalyst, if used) with strong agitation to a temperature in the range of 230 - 350°C and preferably 280 - 340°C. Depending on the melting point of the dicarboxylic component and the chemical nature of the tetraamine and the dicarboxylic component, the liquid mass being agitated will be a slurry, a homogenous mixture or an emulsion of two immiscible liquids. When the viscosity of the reacting mass begins to rise as indicated by increased torque on the agitator manifested by increased energy of agitation, the agitation is discontinued and the mass heated further and allowed to foam. The point at which the agitation is discontinued is generally such that the

agitator torque or energy of agitation has not risen above, for example, about 1000% of the initial torque or agitation energy after the tetraamine has melted, preferably not above about 300% such initial torque or agitation energy. The
5 mass is then heated further without agitation to a temperature in the range, for example, of 230 to 350°C above the melting point of the tetraamine. Such heating is continued for a period of time in the range, for example, of 0.25 to 3 hours and preferably 0.5 to 1.5 hours. The foamed mass
10 is then cooled to a temperature below its melting point, e.g. room temperature, which causes it to set as a solid friable mass which is easily crushed or ground. In general, the inherent viscosity of the prepolymer after the first stage is complete is in the range, for example, of about
15 0.05 to 0.3 dl/g (all inherent viscosities being measured from a solution of 0.4% by weight of polymer in 97% sulfuric acid at 25°C).

The ground prepolymer is then further heated with normal agitation in a second stage at a temperature, for
20 example, of 300 to 420°C, preferably 360 to 400°C, for a period, for example of 0.25 to 4 hours, preferably 0.5 to 2 hours, until the desired degree of polymerization is attained.

When poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole
25 is produced from 3,3',4,4'-tetraaminobiphenyl and an isophthalic component using the monomers and process of this invention, the first stage may be carried out at a temperature of for example, 230 to 350°C, preferably 280 to 340°C, for a period of time, of for example, 0.25 to 3 hours,
30 preferably 0.5 to 1.5 hours.

The two stage process of this invention has processing advantages over one stage processes using a free dicarboxylic acid as monomer proposed previously in
35 which the process is carried out with agitation until the viscosity increase overcomes the torque of the stir motor and locks and/or breaks the agitator. The solid polymer

produced in this manner is generally in the form of a lump which is difficult to remove from the reactor and difficult to process into shaped articles such as fibers.

5 When the dicarboxylic component is free isophthalic acid, it avoids the problems associated with a process (even a two stage process) for the polymerization of diphenylisophthalate with 3,3',4,4'-tetraaminobiphenyl. However, use of isophthalic acid in the previous process which employed diphenylisophthalate has been found to result in
0 polymers of darker color and lower inherent viscosity than those formed with diphenyl isophthalate via this process, or isophthalic acid via the process of this invention.

In addition to the processing advantages made
5 possible by the two stage process of this invention, the process also results in polymers having relatively high inherent viscosities, which is an indication of molecular weight, and relatively high plugging values, which is a filterability measurement indicating the amount of insoluble
0 gels and solid particles present in the polymer.

In both stages of the process of the present invention, a pressure is employed which is preferably substantially equal to or greater than atmospheric pressure, e.g. one to two atmospheres, and most preferably atmospheric
5 pressure. Such a pressure is commonly obtained by employing an open polymerization system provided with a condenser in order to remove the compounds which are produced as by-products of the reaction.

Both stages of the process may be conducted in
a substantially oxygen-free atmosphere. For example, an inert gas such as nitrogen or argon can be continuously passed through the reaction zone during the polymerization. The inert gas employed should be substantially oxygen-free, i.e. it should contain less than 20 p.p.m. of oxygen, preferably less than 8 p.p.m., and more preferably, be entirely
oxygen-free. The inert gas may be introduced into the

reaction zone at a rate of flow measured at standard conditions, that is, atmospheric pressure and temperature, 1 to 200 percent of the volume of the reaction zone per minute. The inert gas may be passed into the polymerization reaction
5 zone at room temperature or, if desired, it may be pre-heated to the reaction temperature.

The process of the present invention can be used to produce a high molecular weight polybenzimidazole product as indicated by relatively high inherent viscosity. Such
10 products exhibit an inherent viscosity of, for example, at least 0.4 dl/g when measured at a concentration of 0.4 g. of the polymer in 100 ml. of 97 percent H_2SO_4 at 25°C. Preferably, the polymer exhibits an inherent viscosity of
15 at least 0.5 dl/g, and the inherent viscosity is most preferably at least 0.6 dl/g.

The following Examples further illustrate the invention. The inherent viscosities mentioned in the examples were measured as a 0.4% solution in 97% concentrated sulfuric acid at 25°C while the plugging values were
20 measured by forming a 5% solution of the polymer in 97% sulfuric acid or a 6% solution in dimethyl acetamide containing 2% lithium chloride and filtering the solution at 25°C and one atmosphere pressure through a Gelman Type A
25 gloss paper filter. The plugging value, which is the number of grams of polymer solution filtered per unit area in infinite time, is expressed in grams of polymer per square centimeter. A higher value indicates a polymer solution containing less gels and insolubles.

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Into a four-necked, one-liter, round bottomed flask equipped with a nitrogen inlet and outlet, a mechanical stirrer, a thermocouple and a condenser was placed 30.0 g (0.181 mol) of isophthalic acid and 38.7g (0.181 mol) of 3,3',4,4'-tetraaminobiphenyl and 2.2 g (7.2 mmol) triphenylphosphite. The flask was degassed and filled with nitrogen. The degassing was repeated at least three times. The flask was then heated with an oil bath at 350°C/hr to 300°C. Stirring was maintained at 300 rpm until condensate evolution began to slow and a rapid torque increase on the stir motor was seen. Stirring was terminated when the torque increased to 150 mV from a value before viscosity increase of 30mV. The oil and polymer temperatures were 270°C and 242°C, respectively, at this point. The oil bath temperature was increased to 300°C and held at that temperature for one hour. The foam height in the flask was 10.0 cm. The initial height of reactants in the flask was approximately 1.5 cm. The resulting product was cooled to room temperature and then was ground. The ground prepolymer was placed in a flask, the degassing cycles described above were repeated, and the prepolymer was heated with stirring at 60 rpm at 380°C for 1.5 hours. The resulting polybenzimidazole exhibited an inherent viscosity of 0.63 dl/g and a dimethylacetamide (DMAc) plugging value (PV) of 1.83 g/cm.

As a control, the polybenzimidazole of this example was prepared according to the procedure described except that agitation of the initial heating step terminated at an oil and polymer temperature of 250° and 222°C, respectively, and agitation was terminated before viscosity began to build as evidenced by constant torque readings on the agitator motor. The first stage foam height was 5.5 cm. The resulting polybenzimidazole exhibited an inherent viscosity of 0.44 dl/g and a dimethylacetamide (DMAc) plugging value (PV) of 1.05 g/cm.

EXAMPLE II

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The procedure of Example I was repeated and stirring was terminated when the torque increased to approved 120 mV from a value before viscosity increase of 30 mV. The first stage was heated to 300°C and held at that temperature for 1 hour. The second stage was heated to 380°C and held at that temperature for 2 hours. The resulting polybenzimidazole exhibited an inherent viscosity of 0.64 dl/g (measured at 0.4% concentration in sulfuric acid), a dimethylacetamide (DMAc) plugging value (PV) of 6.0 g/cm and a sulfuric acid PV of 0.46 g/cm.

EXAMPLE III

The polybenzimidazole of Example II was repeated except that stirring was terminated when the torque increased to 120 mV from a value before viscosity increase of 30 mV, and the first stage was heated to 280°C and held at that temperature for 30 minutes. The second stage was heated to 380°C and held at that temperature for 60 minutes. The resulting polybenzimidazole exhibited an inherent viscosity of 0.62 dl/g (measured at 0.4% concentration in sulfuric acid), a dimethylacetamide (DMAc) plugging value (PV) of 18 g/cm and a sulfuric acid PV of 0.13 g/cm.

EXAMPLE IV

The procedure of Example II was repeated except that stirring was terminated when the torque increased to 120 mV from a value before viscosity increase of 30 mV, and 3.3 g of triphenylphosphite catalyst was used. The resulting polybenzimidazole exhibited an inherent viscosity of 0.57 dl/g (measured at 0.4% concentration in sulfuric acid), a dimethylacetamide (DMAc) plugging value (PV) of 22 g/cm and a sulfuric acid PV of 0.52 g/cm.

The procedure of Example II was repeated except that stirring was terminated when the torque increased to 120 mV from a value before viscosity increase of 30 mV, and 1.1 g of triphenylphosphite catalyst was used. The resulting polybenzimidazole exhibited an inherent viscosity of 0.40 dl/g (measured at 0.4% concentration in sulfuric acid), a dimethylacetamide (DMAc) plugging value (PV) of 22 g/cm and a sulfuric acid PV of 2.5 g/cm.

COMPARATIVE EXAMPLE A

In a control to show the effect of using isophthalic acid in place of diphenylisophthalate in a two-stage polymerization without the novel reaction conditions disclosed in Examples I-V, isophthalic acid, 3,3',4,4'-tetraaminobiphenyl and triphenylphosphite, in the amount of Example I, were placed in a three-necked, round bottomed flask fitted as in Example II. The flask was degassed and filled with nitrogen three times. The flask was then heated with an oil bath at 350°C/hr to 270°C. Stirring was maintained at 60 rpm until condensate began to evolve, at which time agitation was terminated with substantially no increase in torque. Very little foaming was observed. The 270°C temperature was held for 1.5 hours. The resulting product was cooled to room temperature and was ground. The ground prepolymer was placed in a flask, degassed and filled with nitrogen three times, and heated with 60 rpm stirring to 360°C. The temperature was held for 1.0 hours. The resulting polybenzimidazole exhibited an inherent viscosity of 0.40 dl/g (measured at 0.4% concentration in sulfuric acid), and a sulfuric acid PV of 0.20 g/cm.

Yields in the foregoing examples were all greater than 90%.

The procedure of Example I was followed except that certain process conditions were varied. These variations and the properties of the polymers obtained are shown in Table I:

T A B L E I

EXAMPLE	1ST STAGE		2ND STAGE		TPP ¹ (mol %)	IV 1 ² (dl/g)	IV 2 ³ (dl/g)	ACID · PV ⁴ (g/cm ²)	DMAC · PV ⁵ (g/cm ²)
	TEMP (°C)	TIME (hr)	TEMP (°C)	TIME (hr)					
VI	250	0.5	360	1.0	2	0.09	0.37	2.5	22
VII	280	0.5	360	1.0	2	0.11	0.37	2.5	16.9
VIII	280	0.5	380	1.0	2	0.13	0.37	2.5	22
IX	280	0.5	380	1.0	4	0.12	0.62	0.13	18.0
X*	280	0.5	380	1.0	6	0.09	0.57	0.52	22
XI	300	0.5	380	1.0	6	0.16	0.61	0.74	22
XII	320	0.5	380	1.0	6	0.17	0.51	0.42	22
XIII	300	1.0	380	1.5	4	0.16	0.61	0.37	1.9
XIV	300	1.0	380	2.0	4	0.19	0.63	0.43	6.9
XV	300	1.0	380	2.0	4	-	0.60	0.44	-
XVI	300	1.0	380	1.5	4	0.17	0.65	0.39	3.8
XVII	300	1.0	380	1.5	4	0.17	0.64	0.65	3.7
XVIII	300	1.0	380	2.0	4	0.14	0.67	0.46	7.3

¹ Triphenylphosphite.

² First Stage.

³ Second Stage.

⁴ 97% H₂SO₄ a filterability measurement.

⁵ A filterability measurement with N,N-dimethylacetamide.

*Second Stage Polymer Hardened and Locked Agitator.

NOTE: For all runs, initial torque was 30-35 mv. Torque at agitation termination was 90-100 mv.

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COMPARATIVE EXAMPLE B

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First stage foamed prepolymers were synthesized using either (1) isophthalic acid (IPA) according to the procedure in Example II, or (2) diphenylisophthalate (DPIP) according to the procedure in H. Vogel and C.S. Marvel, Journal of Polymer Science, Vol. L., pages 511-539. These materials were compared in Instron compressive crush tests. The average crushing load for the IPA-based foams was 900 to 1000 g. The average crushing load for the DPIP-based foams was 2000 to 3400 g. These results and also the results obtained by crushing a standard type of polyurethane foam are shown in Table 2.

TABLE II

<u>RUN</u>	<u>MATERIAL</u>	<u>CRUSHING LOAD (g)</u>	
		<u>AVERAGE</u>	<u>MAXIMUM</u>
1	Polyurethane Foam 5 x 5 x 1.9	400	1175
2	DPIP-Based Foam 5 x 5 x 2.5	2000	5000
3	DPIP-Based Foam 5 x 5 x 3.8	2000	4100
4	DPIP-Based Foam 3.8 x 3.8 x 3.8	2500	4700
5	DPIP-Based Foam 6.4 x 3.8 x 5	3400	4700
6	IPA-Based Foam 3.8 x 3.8 x 3.8	900	1400
7	IPA-Based Foam 3.8 x 3.8 x 3.8	1000	1700

Instron set at 2"/min(5 cm/min), 5000 g full scale. Dimensions in Table 2 are in inches(cm) (1 x w x t). DPIP foam made in a 11 resin kettle at 270°C for 1.5 hr. IPA -isophthalic acid; DPIP-diphenylisophthalate.

Into a three-necked, one-liter, round bottomed flask equipped with a nitrogen inlet and outlet, a mechanical stirrer and a condenser was placed 10.0g (41.3 mmol) of 4,4'-biphenyldicarboxylic acid, 8.84g (41.3 mmol) of 3,3',4,4'-tetraaminobiphenyl (TAB) and 0.51g (1.65mmol, 4 mol %) triphenylphosphite (TPP). The flask was degassed and filled with nitrogen. The degassing was repeated at least three times. The flask was then heated with an oil bath at 350°C/hr to 280°C. Stirring was maintained at 300 rpm until condensate evolution began to slow the torque increased to 90-100 mV from a value before viscosity increase of 30 mV. The oil bath temperature of 280°C was held for 30 minutes. The resulting product was cooled to room temperature and then was ground. The inherent viscosity (IV) of this first stage product was 0.15 dl/g. The ground prepolymer was placed in a flask, the degassing cycles described above were repeated, and the prepolymer was heated with stirring at 60 rpm at 380°C for 30 minutes. The resulting polybenzimidazole exhibited an inherent viscosity of 0.53 dl/g. The yield was 13.2g (34.5 mmol) or 83%. The polymer was soluble at 6% solids in dimethylacetamide (DMAc)/2% LiCl.

EXAMPLE XX

The procedure of Example XIX was repeated except that 10.0g (41.3 mmol) of 2,2'-biphenyldicarboxylic acid (diphenic acid) was used instead of 4,4'-biphenyldicarboxylic acid and the torque increased to 90-100 mV from a value before viscosity increase of 30 mV. The first stage IV was 0.12 dl/g and the second stage IV was 0.54 dl/g. The isolated yield was 13.4 g (34.8 mmol) or 84%. The polymer was soluble at 6% solids in dimethylacetamide (DMAc)/2% LiCl.

EXAMPLE XXI

0177182

The procedure of Example XX was repeated except that 30.0 g (124 mmol) diphenic acid, 26.5 g (124 mmol) 3,3',4,4'-tetraaminobiphenyl (TAB) and 1.51g (4.9 mmol, 4 mol%) triphenylphosphite (TPP) was used and the torque increased to 90-100 mV from a value before viscosity increase of 30 mV. The first stage was heated to 300°C and held for 60 minutes, and the second stage was heated to 380°C and held for 90 minutes. The resulting polybenzimidazole had an IV 0.61 dl/g and a sulfuric acid plugging value (PV) of 0.53 g/cm². The isolated yield was 45.1 g (117 mmol) or 95%.

EXAMPLE XXII

The procedure of Example XXI was repeated except that the first stage was heated to 340°C and held at that temperature for 60 minutes. The second stage was heated to 380°C and held at that temperature for 90 minutes. The resulting polybenzimidazole exhibited an IV of 0.61 dl/g and a sulfuric acid PV of 0.23 g/cm². The isolated yield was 41.9g (109 mmol) or 88%.

EXAMPLE XXIII

The procedure of Example XXI was repeated except that phenylindandicarboxylic acid (PIDA), also identified as 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-trimethyl-1H-indene-5-carboxylic acid (Chemical Abstract Service registry number 3569-18-4) was used in place of diphenic acid and the torque increased to 90-100 mV from a value before viscosity increase of 30 mV. The weights used were 30.0 g (92.6 mmol) phenylindandicarboxylic acid (PIDA), 19.8 g (92.6 mmol)

3,3',4,4'-tetraaminobiphenyl (TAB) and 1.14 g (3.81 mmol, 4 mol %) triphenylphosphite (TPP). The first stage polymer had an IV of 0.12 dl/g, and the second stage polymer had an IV of 0.63 dl/g and a sulfuric acid PV of 2.5 g/cm². The isolated yield was 41.4 g (88.8 mmol) or 96%. The polybenzimidazole produced was soluble at 6% solids in dimethylacetamide (DMAc)/2% LiCl.

EXAMPLE XXIV

Into a three-necked, one-liter, round bottomed flask equipped with a nitrogen inlet and outlet, a mechanical stirrer, and a condenser were placed 29.29g (90.40 mmol) of phenylindan dicarboxylic acid (PIDA), also identified as 3-(4-carboxyphenyl)-2,3-dihydro-1,1,3-dihydro-1,1,3-trimethyl-1H-indene-5-carboxylic acid (Chemical Abstract Service registry number 3569-18-4), 28.75g (90.41 mmol) of diphenyl isophthalate (DPIP), 38.68g (180.8 mmol) of 3,3',4,4' - tetraaminobiphenyl (TAB) and 2.27g (7.31 mmol) of triphenyl phosphite (TPP). The mol % ratio of PIDA to DPIP was 50:50 based on the total dicarboxylic component. The flask was degassed and filled with nitrogen and the degassing was repeated at least three times. The flask was then heated with an oil bath at 350°C/hr to 300°C. Stirring was maintained at 300 rpm until condensate evolution began to slow and the torque increased to 90-100 mV from a value before viscosity increase of 30 mV. The oil bath temperature was held at 300°C for one hour during which time the foam height in the flask increased to 8 cm. from an initial height of reactants in the flask of approximately 1 cm. The resulting first stage product which had an inherent viscosity (IV) of 0.17 dl/g. was cooled to room temperature and then was ground. The ground prepolymer was placed in a flask, and degassing cycles described above were repeated, and the prepolymer was heated with

stirring at 60 rpm at 380C for 1.5 hours. The resulting second stage polybenzimidazole had an inherent viscosity (IV) of 0.51 dl/g and a sulfuric acid plugging value (PV) greater than 5g/cm². The isolated yield was 57.0g or 82%.

EXAMPLE XXV

The procedure of Example XXIV was followed except that a 75:25 mol % ratio of PIDA:DPIP was used. The weights were 43.91g (135.5 mmol) PIDA and 14.38g (45.22 mmol) DPIP. The resulting first stage polymer had an IV of 0.14 dl/g. The resulting second stage polymer had an IV of 0.45 dl/g and a sulfuric acid PV of greater than 5g/cm. The isolated yield was 75.80g or 98%.

EXAMPLE XXVI

The procedure of Example XXIV was followed except that a 67:33 mol% ratio of diphenic acid:DPIP was used. The weights were 21.86g (90.37 mmol) diphenic acid (2,2'-biphenyldicarboxylic acid) and 28.76 (45.22 mmol) DPIP. The resulting first stage polymer had an IV of 0.23 dl/g. The resulting second stage polymer had an IV of 0.89 dl/g and a sulfuric acid PV of 0.06 g/cm.

EXAMPLE XXVII

The procedure of Example XXVI was followed except that about a 75:25 mol% ratio of diphenic acid: DPIP was used. The weights were 30.80g (127.3 mmol) diphenic acid and 14.37 g (45.19 mmol) DPIP. The resulting first stage polymer had an IV of 0.23 dl/g. The resulting second stage polymer had an IV of 0.79 dl/g and a sulfuric acid PV of 0.33g/cm. The isolated yield was 54.8g or 83%.

The polymers of Examples XXIV and XXV are 2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-(1",1",3"-trimethyl-indanylene -5",3"-p-phenylene)-5 5'-bibenzimidazole copolymers, and the polymers of Examples XXVI and XXVII are 2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-(biphenylene-2",2"'')-5,5'-bibenzimidazole copolymers, all of which are new

compositions of matter. The relative number of each benzimidazole unit in the polymer chain depends on the molar ratio of the dicarboxylic compounds used in the polymerization.

Example XXVIII illustrates the process of this invention utilizing a combination of a free dicarboxylic acid and the dimethyl ester of the same acid to form a polybenzimidazole, viz. poly-2,2'(-m-phenylene)-5,5'-bibenzimidazole.

EXAMPLE XXVIII

Into a three-necked, one liter, round bottomed flask, equipped with a nitrogen inlet and outlet, a mechanical stirrer attached to a torque measuring device and a condenser was placed 15.02 g (90.48 mmol) isophthalic acid, 17.55 g (90.46 mmol) dimethyl isophthalate (for a mol% ratio of free acid to dimethyl ester of 50:50), 38.68 g (180.75 mmol) 3,3', 4,4'-tetraaminobiphenyl and 2.25 g (7.26 mmol) triphenyl phosphite. The flask was degassed and filled with nitrogen. The degassing was repeated at least three times. The flask was then heated in an oil bath at 350°C/hr to 300°C. Stirring was maintained at 300 rpm until condensate evolution began to slow and torque on the stir motor had increased from 30 mV to approximately 120mV. At this point agitation was terminated and the polymerizing mass allowed to foam. The oil bath temperature was held at 300°C for 60 minutes. The resulting product was cooled to room temperature and ground. The inherent viscosity of this first-stage product (measured at 0.4% concentration in 97% sulfuric acid) was 0.17 dl/g. The ground prepolymer was placed in a flask, the degassing cycles described above were repeated, and the prepolymer heated with stirring at 60 rpm at 380°C for 90 minutes. The resulting red-brown polybenzimidazole exhibited an inherent viscosity of 0.48 dl/g. The yield was 49 g (159.1 mmol) or 88%.

Examples XXIX, XXX and XXXI illustrate the process of this invention utilizing a combination of dimethyl and diphenyl esters of the same dicarboxylic acid to prepare
5 a polybenzimidazole, viz. the same polymer as Example XXVIII.

EXAMPLE XXIX

The procedure of Example XXVIII was followed with a combination of dimethyl and diphenyl esters of the same
10 dicarboxylic acid in 50:50 mol % ratio. The materials used were : diphenyl isophthalate (28.73 g, 90.35 mmol), dimethyl isophthalate (17.54 g, 90.41 mmol), 3,3',4,4' - tetraaminobiphenyl (38.68 g, 180.7 mmol) and triphenyl phosphite (2.30 g, 7.42 mmol). The resulting first-stage
15 prepolymer had an IV of 0.16 dl/g. The resulting second-stage polymer was dark gold and had an IV of 0.62 dl/g. The yield was 50.8 g (165 mmol) or 91%.

EXAMPLE XXX

20 The procedure of Example XXIX was followed with about 75:25 mol% ratio of dimethyl to diphenyl ester. The materials used were: diphenyl isophthalate (14.37 g, 45.19 mmol), dimethyl isophthalate (28.29g, 145.8 mmol), 3,3',4,4', - tetraaminobiphenyl (38.67 g, 180.7 mmol) and triphenyl
25 phosphite (2.27 g, 7.32 mmol). The resulting first-stage prepolymer had an IV of 0.15 dl/g. The resulting second-stage polymer was dark gold and had an IV of 0.43 dl/g. and a plugging value, as measured in a 5% solution in 97% sulfuric acid, of 0.46 g/cm². The yield was 49.5g (161 mmol)
30 or 89%.

EXAMPLE XXXI

The procedure of Example XXIX was followed with about a 90:10 mol% ratio of dimethyl to diphenyl ester. The
35 materials used were: diphenyl isophthalate (5.79 g, 18.21 mmol), dimethyl isophthalate (31.59 g, 162.8 mmol), 3,3', 4,4' -tetraaminobiphenyl (38.67 g, 180.7 mmol) and triphenyl

phosphite (2.30 g, 7.42 mmol). The resulting first-stage prepolymer had an IV of 0.16 dl/g. The resulting second-stage polymer was dark gold and had an IV of 0.42 dl/g. and a plugging value as measured in a 5% solution in 97% sulfuric acid, of 1.94 g/cm². The yield was 31.5 g (102 mmol) or 57%.

Examples XXXII to XXXV illustrate the preparation of the same polybenzimidazole as was prepared in Examples XXVIII to XXXI using a combination of free dicarboxylic acid and a diphenyl ester of the same acid as the dicarboxylic component of the polymerization.

EXAMPLE XXXII

The procedure of Example XXVIII was followed with about a 50:50 mol% ratio of free acid to diphenyl ester. The materials used were: isophthalic acid (15.02g, 90.41 mmol), diphenyl isophthalate (28.74g, 90.29 mmol), 3,3',4,4'-tetraaminobiphenyl (38.67 g, 180.5 mmol) and triphenyl phosphite (2.26 g, 7.29 mmol). The first stage prepolymer had an IV of 0.20 dl/g. while the second stage polymer had an IV of 0.63. The yield was 55.0 g (179 mmol) or 99%.

EXAMPLE XXXIII

The procedure of Example XXXII was followed with about a 75:25 mol% ratio of free acid to diphenyl ester. The materials used were: isophthalic acid (22.50 g, 135.4 mmol), diphenyl isophthalate (14.38 g., 45.18 mmol) 3,3',4,4'-tetraaminobiphenyl (38.69 g., 180.6 mmol) and triphenyl phosphite (2.26 g, 7.29 mmol). The first stage prepolymer had an IV of 0.17 dl/g. while the second stage polymer had an IV of 0.42 dl/g. The yield was 54.6 g (177.0 mmol), or 98%.

EXAMPLE XXXIV

The procedure of Example XXXII was followed with about a 90:10 mol% ratio of free acid to diphenyl ester.

5 The materials used were isophthalic acid (27.00 g., 162.5 mmol), diphenyl isophthalate (5.75 g, 18.06 mmol), 3,3',3,4'-tetra-aminobiphenyl (38.67g. 180.5 mmol) and triphenyl phosphite (2.24 g, 7.26 mmol). The first stage prepolymer had an IV of 0.17 dl/g. while the second stage polymer had

10 an IV of 0.49 dl/g. and a sulfuric acid PV of 1.4 g/cm². The yield was 52.7 g (171 mmol) or 95%.

EXAMPLE XXXV

The procedure of Example XXXII was followed with about a 95:5 mol% ratio of free acid to diphenyl ester.

15 The materials used were isophthalic acid (28.51 g, 171.6 mmol), diphenyl isophthalate (2.90 g, 9.11 mmol), 3,3',4,4'-tetraaminobiphenyl (38.67 g, 180.7 mmol) and triphenyl phosphite (2.24 g, 7.23 mmol). The first stage prepolymer

20 had an IV of 0.17 while the second stage propolymer had an IV of 0.50 and a sulfuric acid PV of 1.6. The yield was 51.2 g (166 mmol) or 92%.

Example XXXVIII illustrates the process of this invention utilizing a dimethyl ester as the sole dicarboxylic

25 compound.

EXAMPLE XXXVI

This example illustrate the formation of poly-2,2'-(naphthalene -2",6")-5,5'-bibenzimidazole using a dimethyl

30 ester as the sole dicarboxylic component of the polymerization.

The procedure of Example XXVIII was followed using dimethyl-2, 6-naphthalenedicarboxylate as the sole dicarboxylic component except that the first stage was carried

35 out at 340°C for one hour. The materials used were dimethyl-2,6-naphthalenedicarboxylate (38.1 g, 157 mmol), 3,3',4,4'-tetraaminobiphenyl (33.79g, 157.7 mmol) and triphenyl

phosphite (1.95 g, 6.29 mmol). The first stage prepolymer had an IV of 0.27 dl/g. while the second stage polymer had an IV of 0.30dl/g. and a sulfuric acid PV of 2.1 g/cm².

5 The yield was 45.03 g (146.2 mmol) or 93%.

10



CLAIMS

1. A two stage process for providing polybenzimidazoles comprising heating in a first stage a mixture of at least one aromatic tetraamine containing two pairs of amine substituents on an aromatic ring in ortho position and either (i) at least one free dicarboxylic acid or (ii) a dicarboxylic component which is at least one compound having the formula



in which R' is a divalent organic radical (and may be the same or different in the various molecules making up the dicarboxylic component) and the Y's may be hydrogen, aryl or alkyl (provided that no more than 95% of the Y's are hydrogen or phenyl), the said heating being sufficient to bring the mixture to condensation polymerization temperatures above the melting point of the said tetraamine, continuing the heating with agitation until the agitator torque is from about 1.5 to about 6 times the torque before the rise in viscosity begins, terminating the agitation while continuing to heat the reaction mixture to a temperature of from 230 to 350°C while allowing the mass to foam to a substantial degree, cooling to a friable foamed mass, crushing the mass to obtain a ground prepolymer and heating the ground prepolymer in a second stage at a temperature in excess of the highest temperature employed in the said first stage with agitation until an inherent viscosity in excess of 0.37 is obtained.

2. The process of Claim 1 wherein the aromatic tetraamine is 3,3',4,4'-tetraaminobiphenyl.

3. The process of Claim 1 or 2 wherein there is used as free dicarboxylic acid isophthalic acid.

4. The process of Claim 1 or 2 wherein there is used as free dicarboxylic acid diphenic acid and/or 4,4'-biphenyldicarboxylic acid and/or phenylindandicarboxylic acid.

5. The process of Claim 1 or 2 wherein there is used as dicarboxylic component either 1) a combination of at least one free dicarboxylic acid and at least one diaryl ester of a dicarboxylic acid, or 2) a combination of at least one free dicarboxylic acid and at least one dialkyl ester of a dicarboxylic acid, or 3) a combination of at least one diaryl ester of a dicarboxylic acid and at least one dialkyl ester of a dicarboxylic acid; or 4) a dialkyl ester of a dicarboxylic acid.

6. The process of Claim 5 wherein the said dicarboxylic acid is aromatic, the said aryl groups are phenyl, and the said alkyl groups contain 1 to 5 carbon atoms.

7. The process of Claim 5 wherein the said dicarboxylic component is a combination of phenylindandicarboxylic acid and diphenyl isophthalate; or a combination of diphenic acid and diphenyl isophthalate or a combination of isophthalic acid and dimethyl isophthalate, or a combination of isophthalic acid and diphenyl isophthalate or a combination of dimethyl isophthalate and diphenyl isophthalate.

8. The process of Claim 5 wherein the said carboxylic component is dimethyl 2, 6-naphthalenedicarboxylate acid.

9. The process of claim 5 wherein the said dicarboxylic component is dimethyl isophthalate.

10. The process of any of Claims 1 - 9 wherein a catalyst for the reaction is employed.

11. The process of Claim 10 wherein said catalyst is triphenyl phosphate.

12. A 2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-(1"1" 3"-trimethylindanylene-5",-3"-p-phenylene-5,5' -bibenzimidazole copolymer.

13. A 2,2'-(m-phenylene)-5,5'-bibenzimidazole/2,2'-(biphenylene-2"2")-5,5'-bibenzimidazole copolymer.

14. As a new composition of matter. The polybenzimidazole reaction product produced by reacting phenylindandicarboxylic acid with 3,3',4,4'-tetraaminobiphenyl.